

THE EFFECTS OF ALKYLENE GLYCOLS AND THEIR DERIVATIVES ON THE DEHYDRATION OF HIDES AND SKINS*

W. J. HOPKINS, F. P. LUVISI, AND E. M. FILACHIONE

*Eastern Utilization Research and Development Division†
Philadelphia, Pennsylvania 19118*

ABSTRACT

A new approach to the drying and preserving of hides and hide products is presented. Hide pieces treated with water solutions of selected alkylene glycols and alkylene glycol derivatives air-dried with much more whiteness, fiber separation, and suppleness than untreated pieces. Results approach those obtained by the use of solvent dehydration techniques. Compounds that give the described results are listed. An estimation is made of the minimum concentration needed and the effects of concentration on the treatment time needed to give an acceptable air-dried product.



INTRODUCTION

Drying is an acceptable method for preserving perishable animal hides. Presently hides can be dehydrated by air-drying, by treatment with a water-miscible organic solvent of low boiling point, such as acetone or methanol, and by freeze-drying. Air-drying of hides results in a hard, horny mass that is difficult to rehydrate. Solvent dehydration or freeze-drying of hides results in a product that is white, fibrous, flexible, and "open," but economics are one deterrent to use of these two latter processes.

Kremen and Southwood (1, 2) noted an unexpected difficulty in the solvent dehydration of hides which appeared to be caused by condensation of moisture during "desolventization" of hides. The problem was characterized by the appearance of hard, yellow spots on a small percentage of the total surface area of the grain. Tannage generally made the defect more clearly apparent to visual examination. They found that this problem could be overcome by the addition of small quantities of certain solvent-soluble organic materials to the dehydration solvent. These organic materials then protected the hide from condensed water which formed during solvent removal by a "type of tannage." Kremen *et al.* (1)

*Presented in part at the 65th Annual Meeting of the American Leather Chemists Association, Bretton Woods, New Hampshire, June 22-25, 1969.

†Agricultural Research Service, U. S. Department of Agriculture.

stated that the effectiveness of these organic additives was based on the content of certain functional groups, principally hydroxy and ether groups, which have the power to form hydrogen bonds.

The thought occurred to us that such compounds, particularly those that are water-soluble, might serve a similar function in a completely aqueous system and thus one of the difficulties associated with flammable organic solvents, such as acetone, might be avoided. It appeared possible that hides might be impregnated in aqueous solutions of these additives, and this would permit satisfactory drying of the impregnated hide in air.

This paper reports the evaluation of various water-soluble polar compounds as dehydrating agents when used as aqueous impregnants in a pretreatment to air-drying, the types of hide products tested, and the concentrations and methods of treatments.

EXPERIMENTAL

Sources of Hides and Skins

Much of the screening was carried out using depickled grain splits. The commercial pickled grain split was depickled by treating with a 200 percent float containing five percent sodium chloride and five percent sodium acetate. The percentages were based on the pickled weight of the stock. The samples were tumbled for two to three hours in the depickling solution and then washed for two hours in running water.

The fresh skins used in our experiments were samples that came from freshly slaughtered calves. The skins weighed 15 to 18 pounds untrimmed. Any large pieces of flesh and fat were trimmed off at our laboratory.

The bated stock was either prepared at the laboratory by first unhairing hide pieces from fleshed, demanured, brine-cured hides, weighing 25 to 30 pounds, or a side was obtained from a tannery after the bating step.

Screening Methods

Many compounds were tested for their effects on the air-drying properties of hide products and tests were carried out using a variety of substrates, conditions, times, and concentrations. The following methods can be used to summarize this in terms of screening tests. To check a treating agent, a sample of depickled grain split was tumbled for four hours on a laboratory tumbler in a 100 percent float of 20 percent by weight solution of the compound to be tested. In all further references to float, a 100 percent value will be assumed unless another float is specifically mentioned.

To judge the effects of variables such as concentration and treatment time, butyl Carbitol® was used as the treatment and depickled grain split was used as the substrate. The data collected by the above methods can be used to approxi-

mate results which can be expected from other treatments and also from other substrates.

Evaluation

Most of the treatments were carried out in quart jars which were rotated on a tumbler at 18 r.p.m. In a successful treatment, the sample air-dried wholly white and treatments giving such a result were termed acceptable. Whiteness was felt to reflect fiber separation and, as such, indicated an improvement over an untreated sample which dried hard, discolored, and sometimes translucent.

Chrome-Tanning

The effects of some of these treatments on chrome-tanning were checked as follows. Pieces of hide which were unhaired and bated at our laboratory were treated with 20 percent solutions of each of three selected treating agents. These compounds, which were felt to be representative of our treating agents, were butyl Carbitol, ethoxy triglycol, and Carbowax® 600. The hide pieces were treated for two hours by tumbling in the treating solutions and air-dried for seven days at ambient temperatures. Air-dried pieces were rehydrated for six hours statically and then by tumbling overnight. The hide samples were pickled, using 100 percent floats containing ten percent sodium chloride and 1.5 percent sulfuric acid. After tumbling one hour, the pH was taken and further acid was added, if necessary. After another 1/2 hour tumble, the samples were allowed to remain in the float liquor overnight. The next day, the pH was taken and acid added if necessary. Tumbling was continued for one hour. The final pH was 1.7.

Hide pieces were cut from the pickled stock and the following chrome-tanning procedure was followed. Four percent sodium chloride and one percent sodium formate, on the pickled skin weight, were added to a 50 percent float, which was then tumbled with the skin samples for one hour. On the skin weight, an eight percent solution of Tanolin R‡ in a 50 percent float was prepared and this solution was added in three equal feeds at 1/2 hour intervals. After the last addition, tumbling was continued another two hours. A one percent sodium bicarbonate solution was prepared and added periodically. The samples were agitated slowly overnight. The final pH of the supernatant was 4.1. The assay for the chromic oxide content was carried out by following the Official Methods of Analysis of the ALCA, using the alkaline fusion method and titration with sodium thiosulfate (3).

RESULTS AND DISCUSSION

Table I lists those compounds that were tested as aqueous treatments on depickled grain split samples. These compounds were classed as either acceptable (+) or nonacceptable (—), depending upon whether the treated samples air-

‡Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

TABLE I
THE EFFECT OF ALKYLENE GLYCOLS AND THEIR DERIVATIVES
ON THE AIR-DRYING OF DEPICKLED GRAIN SPLIT

Compound	Chemical Formula	Acceptability*
Ethylene glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$	—
Methyl Cellosolve	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	—
Ethyl Cellosolve	$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$	—
Methyl Cellosolve acetate	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OOCCH}_3$	—
Hexylene glycol	$\text{CH}_3\text{CHOHCH}_2\text{C}(\text{OH})(\text{CH}_3)_2$	+
Diethylene glycol	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	—
Methyl Carbitol	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	—
Ethyl Carbitol	$\text{C}_2\text{H}_5\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	—
Butyl Carbitol	$\text{C}_4\text{H}_9\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$	+
Diethyl Carbitol	$\text{C}_2\text{H}_5\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5$	+
Carbitol acetate	$\text{CH}_3\text{COO}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5$	+
Triethylene glycol	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{H}$	—
Methoxy triglycol	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{H}$	+
Ethoxy triglycol	$\text{C}_2\text{H}_5\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{H}$	+
Propylene glycol	$\text{CH}_3\text{CHOHCH}_2\text{OH}$	—
Dipropylene glycol	$\text{CH}_3\text{CHOHCH}_2\text{OCH}_2\text{CHOHCH}_3^\dagger$	—
Tripropylene glycol	$\text{CH}_3\text{CHOHCH}_2\text{OCH}_2\text{CH}(\text{CH}_3)\text{OCH}_2\text{CHOHCH}_3^\dagger$	+
Dipropylene glycol methyl ether	$\text{CH}_3\text{O}(\text{C}_3\text{H}_6\text{O})_2\text{H}$	+
Tripropylene glycol methyl ether	$\text{CH}_3\text{O}(\text{C}_3\text{H}_6\text{O})_3\text{H}$	+
Glycerol	$\text{CH}_2\text{OHCHOHCH}_2\text{OH}$	—
1,2,6-Hexanetriol	$\text{HOCH}_2\text{CH}(\text{OH})\text{C}_4\text{H}_9\text{OH}$	—
Carbowax 200	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$	—
Carbowax 300	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$	+
Carbowax 400	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$	+
Carbowax 600	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$	+
Carbowax 1000	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$	+
Carbowax 1500	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$	—
Carbowax 1540	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$	—
Carbowax 550	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$	+
Carbowax 750	$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$	+

*The treated specimens of hide were evaluated after air-drying for the degree of fiber separation as judged from whiteness and fiber nature.

+ = acceptable; — = unacceptable.

†And other isomers.

dried wholly white (or creamy white) or not. It was felt that such ratings were adequate for screening purposes.

The selection of glycols and glycol derivatives used was based on high water solubility and commercial availability.

These compounds which gave acceptable screening results were also suitable when used as treatments on depickled cabrettas or on bated stock. Freshly flayed stock, however, generally required a longer treatment time than other substrates and did not always respond as favorably as depickled or bated stock. Some of the compounds that were tried on small samples of fresh calfskins and gave an acceptable dried product were butyl Carbitol, ethoxy triglycol, Carbitol acetate, Carbowax 550, and Carbowax 1000.

The compounds listed in Table I have also proved successful for treatment of tanned substrates. Tanned stock treated with the compounds of Table I are air-dried to give softer and more flexible products than untreated pieces. Treatment levels as low as 5.0 percent by weight solutions were effective in this application.

An experiment was set up to get some idea of the minimum concentration of these compounds needed to give an air-dried product that was white and fibrous. The experiment was also designed to point out whether the concentration of treatment per weight of skin or the treatment strength in the final solution would determine what was the minimum concentration. The term "final solution" was defined as the strength of the butyl Carbitol solution calculated on the basis of the float solution plus the water present in the skin. Assuming an equilibration of the butyl Carbitol between the float and the water in the skin, it reflects the amount of butyl Carbitol picked up by the hide sample when it is removed from solution.

TABLE II
INFLUENCE OF CONCENTRATION OF BUTYL CARBITOL (BC)
ON AIR-DRYING OF IMPREGNATED HIDE*

	I	II	III	IV	V
Expt. No.	BC Stock Solution (Wt.-%)	Float (%)	Grams BC per 100 Grams DPGS	Grams BC per 100 Grams Final Sol'n†	Acceptability‡
1	5	50	2.5	1.9	Very poor
2	5	100	5.0	2.8	Very poor
3	5	200	10.0	3.6	Poor
4	10	50	5.0	3.9	Poor
5	20	25	5.0	4.8	Fair
6	10	100	10.0	5.6	Acceptable

*The substrate used was depickled grain split. Samples tumbled for 7.5 hours. BC stands for butyl Carbitol.

†Calculated on basis of total solution, *i.e.*, the float plus water in the skin (assuming 80 percent water in the skin).

‡Acceptability was based on a sample that dried wholly white.

Table II presents the data collected from this experiment. There is a direct correlation between Column IV and acceptability. As the concentration of butyl Carbitol (grams per 100 grams of total solution) increases from a value of 1.9 up to 5.6, the acceptability level improves from poor up to acceptable. The data also show that a final solution strength of 5.6 grams of butyl Carbitol per 100 grams is an approximation of the minimum butyl Carbitol concentration needed to give an acceptable air-dried product. This criteria is met by a 100 percent float of a ten percent by weight solution of butyl Carbitol. Experience has shown that this concentration criteria generally holds true for other acceptable treatment additives besides butyl Carbitol. Dipropylene glycol methyl ether (DPM) is an example of one treating agent which did not give acceptable results at the ten percent treating level but was acceptable at the 20 percent level of treatment.

The effects of concentration of reagent on the tumbling time necessary to give an acceptable sample for air-drying are described by the following experimental results.

At the 30 percent level of treatment, air-dried samples of depickled grain splits were acceptable after five minutes of tumbling. Further tumbling did not show any improvement in terms of flexibility. At the 20 percent level, samples were acceptable after five minutes, although they were stiffer than samples taken at a later time. The ten percent treatment gave acceptable samples after 15 minutes but these samples, even after eight hours of tumbling, were less flexible than those treated at the higher concentrations. A five percent level of treatment was unsatisfactory at all treatment times. These data can be summed up as follows: the higher the concentration of reagent, the shorter the treatment time needed to give acceptable results. This appeared to be true whether the treating conditions were static or dynamic.

TABLE III
CHROMIC OXIDE CONTENT AND SHRINK TEMPERATURE
OF CHROME-TANNED LEATHER*

Sample Pretreatment	Cr ₂ O ₃ Content Dry Basis (%)	Shrink Temperature (°C.)
Ethoxy triglycol	3.08	92
Butyl Carbitol	3.18	92
Carbowax 600	3.12	92
Control	3.35	92

*Prepared from a fleshed, demanured, salt-cured hide which was unhaired and bated at our Laboratory. After bating, the samples were treated by tumbling two hours with 20 percent by weight solutions of the treating agent and then allowed to air-dry for seven days. The samples were then rehydrated and chrome-tanned.

Table III shows the Cr_2O_3 contents and the shrink temperatures of leathers which were made from hide samples that had been treated after the bating step and then air-dried, rehydrated, pickled, and chrome-tanned. The control sample was pickled directly after bating and chrome-tanned. There does not appear to be any great difference between the individual values of Cr_2O_3 content or T_s , nor did the general appearance of the treated samples differ to any great extent from that of the control. The results indicate that these dehydration treatments do not interfere with the chrome uptake and its effects on the shrink temperature of the tanned stock.

CONCLUSIONS

Our findings show that the treatment of hides and hide products with water solutions of certain alkylene glycols and alkylene glycol derivatives results in a product that air-dries with much more whiteness and suppleness than an untreated sample. It appears to be necessary to use a certain minimum concentration of the additive to insure that an effective concentration of additive remains in the sample to give a wholly white sample. These treatments do not appear to interfere with the chrome-tanning process.

The commercial usefulness of this method as a replacement for present curing or preservation methods used does not seem feasible when one considers the economics involved. However, this process offers a means of preservation of beamed hides without the need for pickling. The dry stock could be stored without the need of refrigeration and much of the weight of the wet hide would be eliminated. The dry beamed sides would then be available for possible tannage or impregnation by aqueous or solvent methods. Since the use of these compounds on products such as chrome- and glutaraldehyde-retanned leather also aids in their drying back softer and more flexible than untreated material, the possibility of their use as a means to reduce the amount of staking needed to soften leather might be of interest.

ACKNOWLEDGMENT

The authors are grateful to Union Carbide Corporation and the Dow Chemical Company for supplying samples of alkylene glycols and their derivatives.

REFERENCES

1. Kremen, S. S., and Southwood, R. L. *JALCA*, **55**, 24 (1960).
2. Kremen, S. S., and Southwood, R. L. U. S. Patent 2,917,833 (December 22, 1959).
3. Official Methods of Analysis, ALCA, 1957. May be secured from the Secretary-Treasurer of ALCA, Tanners' Council Research Laboratory, University of Cincinnati, Cincinnati, Ohio 45221.

DISCUSSION

MR. BATTLES: This paper will be reviewed by Mr. Presley of Eagle-Ottawa Leather Co.

MR. PRESLEY: Thank you, Mr. Hopkins, for this very thought-provoking paper. Its content is certainly in keeping with the key of our convention this year: "1984, Today's Tomorrow." As you stated, this is a novel approach to the dehydration of hide, but it's strictly in the research stage. Despite the fact that little work along this line of endeavor has been published, it would be safe to say that many in this room right now are seriously contemplating or thinking of possible application of these materials somewhere in their tanning processes.

I have had the opportunity to look over the sample swatches that Mr. Hopkins has here. You all should prevail upon yourselves to take the time to look them over. You will find them most interesting.

I would like to ask Mr. Hopkins a question in regard to the economic aspect.

MR. HOPKINS: The cost of the polyethylene glycols that we found to be successful as treatments was around 30 cents a pound per drum lot. This is expensive when one considers that at least ten percent, based on the weight of the side, is required. The results are novel and it is possible that the price may come down. These compounds and their effects on hide material may prove interesting enough to find use in a specialty application, but I don't think it will be able to compete as a preservation technique, since the trend is toward the use of fresh hides without any cure whatsoever. However, the hides can be kept without refrigeration, if it were feasible to put them in this condition.

MR. PRESLEY: Are there any questions from the floor? Please state your name and company affiliation.

DR. WILLIAM PRENTISS (Rohm and Haas Company): Mr. Hopkins, do you have any indication that the glycol ethers are retained at all by the hide substance during the processing through to the finished leather?

MR. HOPKINS: No, we haven't.

MR. CLINT RETZSCH (Nopco Chemical Division, Diamond-Shamrock Corporation): Have you determined the amount of pick-up of your material from the treating bath? In other words, if there's just a certain portion picked up, can you replenish the bath and use it again, which, of course, will bring the cost down considerably?

MR. HOPKINS: Yes, I've tried a few experiments along these lines, and I believe this could be done.

MR. PRESLEY: Any other questions? . . . Well, thank you very much, Mr. Hopkins.